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| 著者 | Ashino Tetsuya, Takada Kunio, Morimoto Yukitoshi, Yasuhara Hisao, Kurosaki Mayuko, Abiko Kenji |
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Determination of Trace Amounts of Carbon in High-Purity Iron by Infrared Absorption after Combustion: Pretreatment of Reaction Accelerator and Ceramic Crucible

Tetsuya Ashino¹, Kunio Takada¹, Yukitoshi Morimoto², Hisao Yasuhara³,
Mayuko Kurosaki⁴ and Kenji Abiko¹

¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

²Japan Analyst Corp., Tokyo 141-0031, Japan

³Technical Research Lab., Kawasaki Steel Corp., Chiba 260-0835, Japan

⁴Japan Energy Analytical Research Center Co. Ltd., Toda, Saitama 335-0021, Japan

Pre-treatment procedures for analysis for determination of trace carbon amounts in high-purity iron was investigated. Carbon in metal samples has been determined with an infrared absorption method after combustion. An analytical sample with a mixed tungsten-tin as a reaction accelerator in a ceramic crucible is subjected to combustion in oxygen atmosphere. Contamination carbon species in the oxygen gas, the ceramic crucible and the accelerator cause analytical blank value. The oxygen gas was purified. The ceramic crucible was heated at 1623 K for more than 20 min in ambient atmosphere. Moreover, the accelerator was heated in ambient atmosphere at 1003 K for 15 min with stirring it every 5 min during heating. Consequently, the carbon blank could be completely removed, and trace amounts of $\mu\text{g}\cdot\text{g}^{-1}$ level carbon in high-purity iron could be determined in the proposed method.

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Keywords: high-purity iron, determination of trace amounts of carbon, infrared absorption after combustion, removal of blank value

1. Introduction

The concentration of impurity elements in high-purity metals have been decreased according to development of technologies for production. The characteristics of high-purity metals are influenced by the trace impurity elements in them. New techniques for the determination of trace elements are needed so that the impurity elements in high-purity metals can be estimated more accurately. Especially, development of determination procedure for trace amounts of carbon and other gaseous elements (S, O, N, and H) in high-purity metal are required.

It is necessary to concern the following points for determination of trace amounts of gaseous elements in metal samples. For example, adsorbed or reacted gaseous species exist on an analytical sample surface. Moreover, instruments to analyze are contaminated with ambient atmosphere. These contamination species cause blank values in determination of gaseous elements. Thus, precise and sensitive analytical values cannot be obtained. Because, a blank signal overlaps on an analytical signal contained within the sample. Accordingly, pre-treatment procedures to decrease and stabilize of blank values are needed to obtain better reliability on the analytical values.

An infrared absorption method after combustion in an oxygen atmosphere has been employed for determination of carbon contents in metal sample.¹⁻³⁾ Carbon species in metal samples are converted into carbon dioxide by combustion in oxygen atmosphere. Two types of combustion furnace are employed for determination of carbon in metals. One is an induction furnace, the other is a tube furnace. Mixture of tungsten and tin for combustion in the induction furnace, or tin only for combustion in the tube furnace is employed as reaction accelerator. In this work, the induction furnace for

sample combustion with the tungsten-tin mixed accelerator was employed. Both an analytical metal sample and the accelerator are insert into a ceramic crucible, after that, they are ignited in the combustion furnace and subjected to combustion. Finally, content of converted carbon dioxide is measured with infrared absorption method.

As well as determination method for other gaseous elements, pre-treatment methods before analysis are needed for precise and sensitive determination of trace amounts of carbon in high-purity iron. Because, analytical values are affected by contaminated carbon species which exist on an analytical sample surface, in the oxygen gas, the ceramic crucible and the accelerator. Therefore, The oxygen gas is purified through a copper (II) oxide column, and the ceramic crucible is heated to remove the carbon species in them. Removal methods of carbon species on surface of sample have been reported.^{4,5)} Moreover, the authors have been investigated that the accelerator was heated in ambient atmosphere before analysis to decrease of the carbon species in the accelerator.⁶⁾ These procedures are important for determination of trace amounts of carbon in high-purity iron.

In order to decrease and stabilize of the carbon blank, the removal method of carbon species in the oxygen gas, the ceramic crucible and the accelerator was investigated. Next, trace amounts of carbon in high-purity iron samples were determined and the proposed procedure was verified.

2. Experimental

2.1 Principle of infrared absorption after combustion

A principle of analytical procedure with infrared absorption method after combustion is shown in Fig. 1. First, an oxygen gas is purified. An oxygen gas flows through a heated copper (II) oxide column, after then, is introduced into a

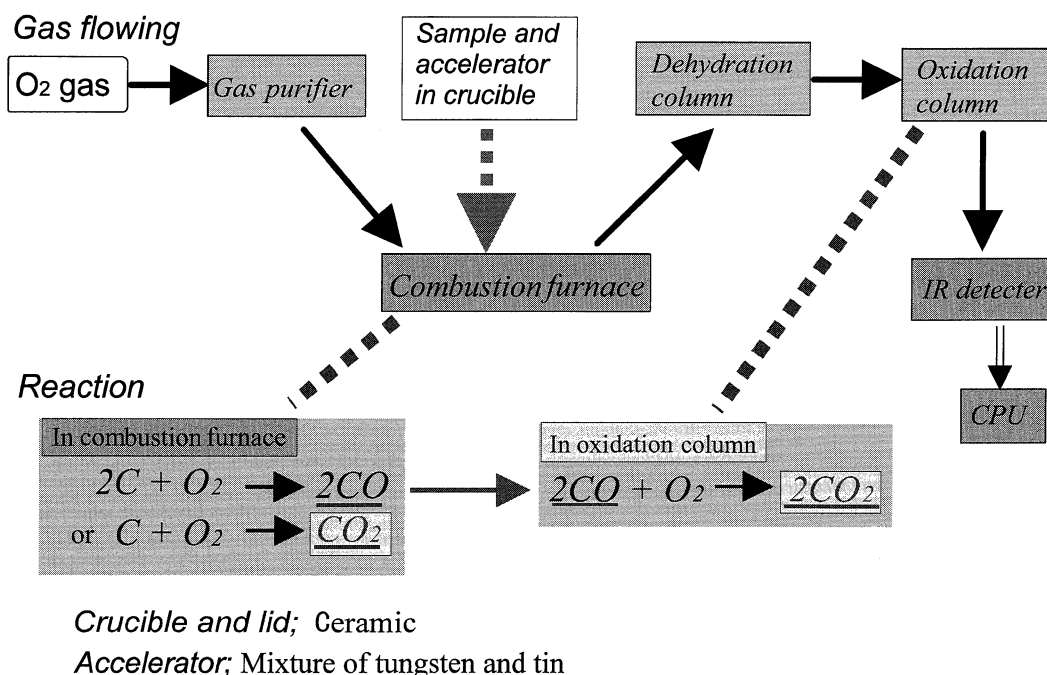


Fig. 1 Flow chart of carbon analysis with infrared absorption method after combustion.

reagent column for removal of water and carbon dioxide. A sample and an accelerator in a ceramic crucible are inserted into a combustion furnace and subjected to combustion in the purified oxygen atmosphere. Then, most of the carbon species in the sample are converted into carbon dioxide, and parts of them are converted into carbon monoxide. Next, they flow through a dehydration column, and into an oxidation column. Carbon monoxide is oxidized into carbon dioxide in the oxidation column. Accordingly, the carbon species in sample are completely converted into carbon dioxide. Finally, the carbon dioxide is introduced into an infrared detector, and the carbon dioxide content is measured by infrared absorption method.

2.2 Apparatus

A LECO CS-444 LS carbon and sulfur analyzer with an induction furnace was employed and the operating conditions are listed in Table 1. A LECO TF-1 tube furnace for heating of a ceramic crucible and its lid, and a Yamato FP-1 muffle furnace for heating of an accelerator were employed. Both a LECO CF-10 gas purifier and a purifier equipped in LECO CS-444 LS were employed for purification of an oxygen gas.

2.3 Reagent

Reagents for determination of carbon with LECO CS-444 LS are listed as follows: Copper Oxide Catalyst (LECO Corp.) as a catalyst for purification of an oxygen gas, Anhydron (LECO Corp.) as a reagent for removal of water, and Lecosorb (LECO Corp.) as a reagent for removal of carbon dioxide, Platinum/Silica Catalyst (LECO Corp.) as a catalyst for oxidation of carbon monoxide into carbon dioxide. A mixture of 1.5 g of Lecocel II HP (main component; tungsten) and 0.5 g of tin metal (LECO Corp.) was used as a reaction accelerator for combustion of samples. A used oxygen gas purity was more than 99.99%.

Table 1 Instruments and operating conditions.

| | |
|---------------------------------|---|
| Analyzer | Leco CS-444 LS |
| Combustion furnace | Induction furnace |
| Frequency | 18 MHz |
| Power | 2.2 kW |
| Detection | Infrared absorption |
| Oxygen gas | |
| Pressure | 2.4×10^5 Pa |
| Flow rate | 2.5 L min^{-1} |
| System operation | |
| Purge time | 30 sec |
| Delay time | 60 sec |
| Detection time | 50 sec |
| Accelerator | |
| Lecocel II HP | 1.5 g |
| Tin metal | 0.5 g |
| Standard sample for calibration | Japan Analyst Corp. 001-051 (C: $78 \pm 5 \mu\text{g}\cdot\text{g}^{-1}$) |
| Furnace for heating of crucible | Leco TF-1 (Tube furnace) |
| Temperature | 1623 K |
| Purifier of oxygen gas | Leco PF-10 |
| Temperature | 1123 K |

2.4 Sample

Six kinds of samples for determination of trace amounts of carbon contents are listed as follows: a high-purity electric iron A-Iron, Mairon HP (Toho Zinc Co. Ltd.), a Japanese Iron and Steel Certified Reference Materials JSS 001-4 (C:

$2.5 \mu\text{g}\cdot\text{g}^{-1}$), 003-4 (C: $6 \mu\text{g}\cdot\text{g}^{-1}$), 1201-1 (C: $5 \mu\text{g}\cdot\text{g}^{-1}$) and a High Purity Iron Chip LECO 502-231 (C: under $8 \mu\text{g}\cdot\text{g}^{-1}$, LECO Corp.). Calibration Standard Sample JAC 001-051 (C: $78 \pm 5 \mu\text{g}\cdot\text{g}^{-1}$, Japan Analyst Corp.) was used for calibration of the analyzer.

2.5 Procedure for sample cleaning

The authors adopted "mixture of HF and H_2O_2 cleaning method⁶⁾" for preparation of iron samples. The procedure is explained as follows. Block iron samples were chemically etched for 1 min in a mixture of hydrofluoric acid (7.5 cm^3), hydrogen peroxide (125 cm^3) and distilled water (15 cm^3), which had been cooled at 273 K before use. Immediately, the chemical-etched samples were transported to a mixture of hydrogen peroxide (50 cm^3) and distilled water (50 cm^3) and etching reaction was stopped. After then, the samples were washed for 1 min in distilled water and ethanol with an ultrasonic cleaner, respectively. Finally, the samples were dried in ambient atmosphere at room temperature.

2.6 Procedure for determination of carbon

A schematic procedure for determination of trace amounts of carbon in high-purity iron is shown in Fig. 2, and a pre-treatment procedure for removal of carbon species in a ceramic crucible and an accelerator is shown in Fig. 3. The procedure is explained as follows. First, a ceramic crucible and its lid was insert into a tube furnace and heated in ambient atmosphere at 1623 K for more than 20 min. Then, an accelerator for combustion was added into the heated crucible. Next, the accelerator in the ceramic crucible and the lid were put into a muffle furnace and heated in ambient atmosphere at 1003 K for 5 min. After heating for 5 min, the heated accelerator in the crucible was taken out from the muffle furnace, and was vigorously stirred with platinum wire for 10 sec. Then, it was again put into the muffle furnace. These operations were repeated 3 times, that was, the heating time was 15 min in total. After heating of accelerator, the heated accelerator in the crucible was taken out from the muffle furnace. After 10 sec, sample was set on the hot accelerator, and was stood for 1 min. Finally, it was inserted into an induction furnace,

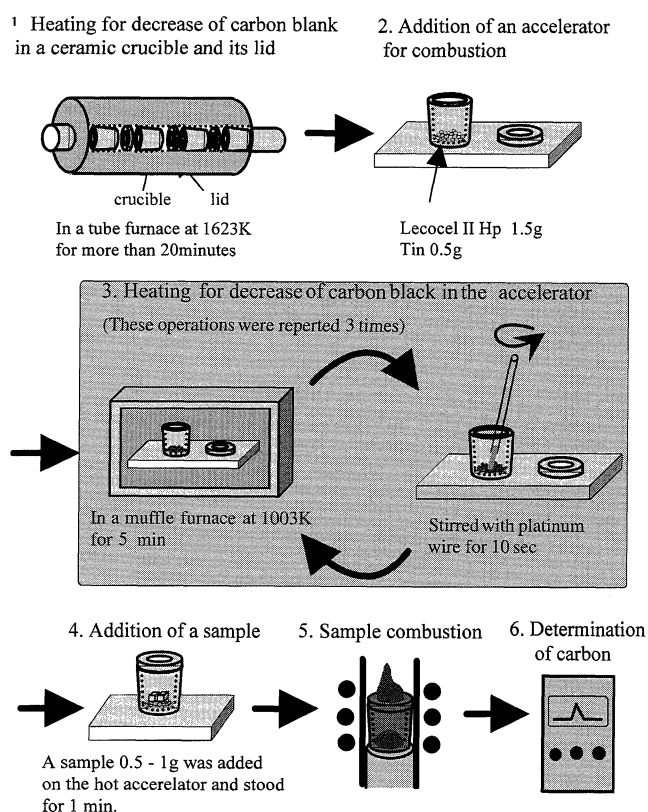


Fig. 3 Removal procedure of carbon blank in reaction accelerator and ceramic crucible.

and carbon amounts were determined. Determination of carbon blank was performed without an analytical sample described the proposed procedure.

3. Results and Discussions

3.1 Effect of heating temperature of accelerator

Effects of heating temperature on the analytical blank value in the heating temperature range between 473 and 1073 K were investigated. The relationship between the heating tem-

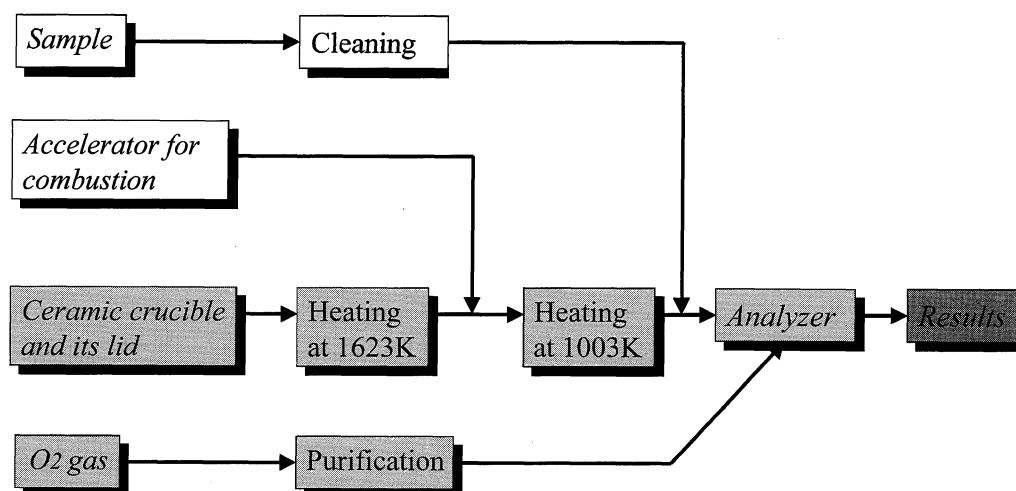


Fig. 2 Flow chart for determination of carbon.

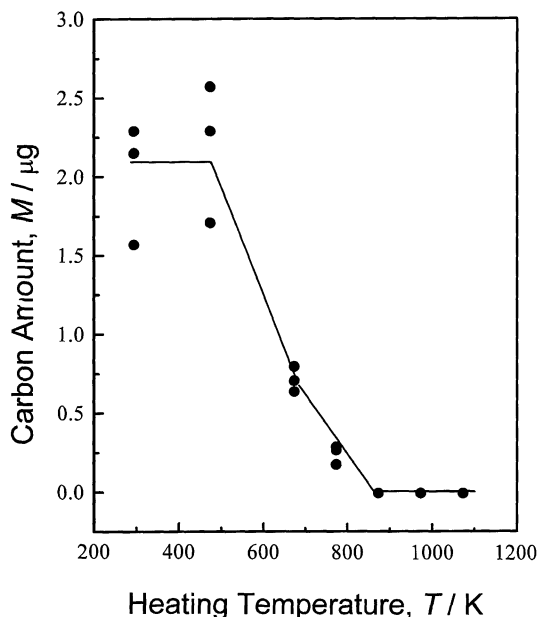


Fig. 4 The relationship between the heating temperature and carbon amount in accelerator: Lecocel II HP 1.5 g+tin 0.5 g; Heating time; 15 min.

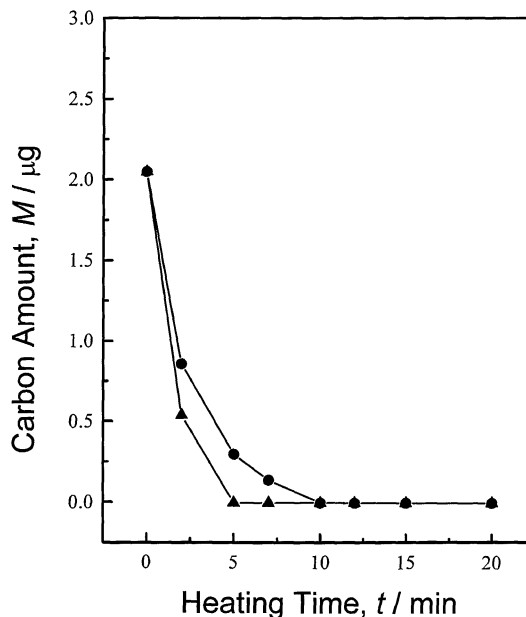


Fig. 5 The relationship between the heating time and the carbon amount in accelerator: Lecocel II HP 1.5 g+tin 0.5 g, Heating temperature; —●— 903 K, —▲— 1003 K.

perature and the carbon amounts in accelerator is shown in Fig. 4. The investigated heating time of accelerator was 15 min. As a result, the carbon content in accelerator was decreased following with rise of heating temperature. Moreover, the obtained carbon content was zero at high temperature than 873 K. On the other word, the analytical carbon blank values could be completely removed with heating the accelerator at high temperature than 873 K for 15 min.

3.2 Effect of heating time of accelerator

Next, effects of heating time on the analytical blank value were investigated. The relationship between the heating time and the carbon amounts in accelerator is shown in Fig. 5. As a result, the obtained carbon amount contained in the heated ac-

celerator at 903 K showed zero for more than 10 min. Moreover, the obtained carbon amount contained in the heated accelerator at 1003 K showed zero for more than 5 min. Consequently, according to the heating at high temperature, the analytical carbon blank found to be completely removed for a short time.

3.3 Effect of heating of crucible and stirring of accelerator

Effects of heating a ceramic crucible and stirring of accelerator on analytical blank values were investigated. The results are listed in Table 2. The carbon blank value was greatly decreased with employing the heated ceramic crucible at 1623 K, compared with the case where the crucible

Table 2 Effects of heating of crucible and stirring of accelerator on carbon blank values.

| | Carbon values | | | |
|--------------------------|---------------|-------|-------|------|
| | μg | | | |
| Heating of crucible* | no | yes | yes | yes |
| Heating of accelerator** | no | no | yes | yes |
| Stirring*** | no | no | no | yes |
| 1 | 39.36 | 2.44 | 0.22 | 0.00 |
| 2 | 32.79 | 3.47 | 0.11 | 0.00 |
| 3 | 35.63 | 2.66 | 0.08 | 0.00 |
| 4 | 38.81 | 2.95 | 0.12 | 0.00 |
| 5 | 28.20 | 2.36 | 0.26 | 0.00 |
| Average | 34.96 | 2.78 | 0.16 | 0.00 |
| SD | 4.61 | 0.45 | 0.08 | |
| RSD (%) | 13.19 | 16.22 | 49.11 | |

*; at 1623 K for more than 20 min,

**; at 1003 K for 15 min,

***; stirred every 5 min (3 times) during heating of accelerator.

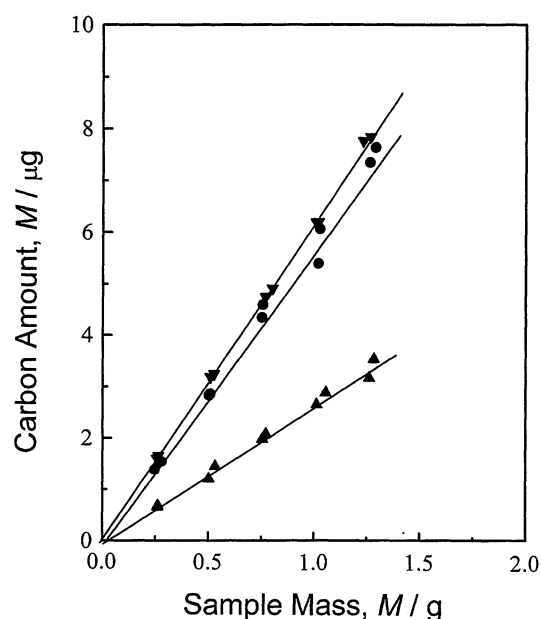


Fig. 6 The relationship between the sample mass and carbon amount JSS sample: ● JSS 1201-1, ▲ JSS 001-4, ▼ JSS 003-4.

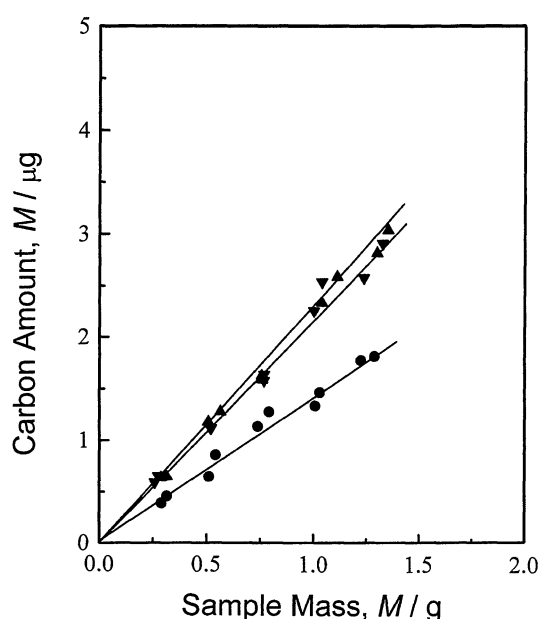


Fig. 7 The relationship between the sample mass and carbon amount in high-purity iron: ● A-ion, ▼ Leco 502-231, ▲ Mairon HP.

was not heated. This data explains the existence of carbon species contained in the non-heated ceramic crucible. Accordingly, the necessity of heating of the ceramic crucible was confirmed.

Then, the carbon blank value was further decreased with employing the heated and non-stirred accelerator at 1003 K within the heated crucible at 1623 K. However, it could not be completely removed when the accelerator was not stirred. However, the blank value could be completely removed when not only the crucible and the accelerator were heated, but also accelerator was stirred every 5 min during heating of accelerator. Therefore, the authors adopted that the accelerator was heated in ambient atmosphere at 1003 K for 15 min, and the

accelerator had to be stirred every 5 min during heating.

3.4 Determination of carbon in changed sample mass

Carbon contents in six kinds of high-purity iron samples were determined in changed the sample mass according to the proposed procedure. The relationships between the sample mass and the analytical carbon amounts were plotted, and calculated by the least-squares method. A slope of straight-line describes the carbon content in sample, and an intercept of Y-axis describes the analytical carbon blank value. Three kinds of JSS Certified Materials were determined and the relationship between the sample mass and the analytical amounts of carbon is shown in Fig. 6. Next, three kinds of high-purity

Table 3 Analytical results of carbon in high-purity iron samples.

| Sample | Certified value $\mu\text{g}\cdot\text{g}^{-1}$ | Carbon found $\mu\text{g}\cdot\text{g}^{-1}$ (slope) | Blank value μg (Intercept of Y Axis) | Coefficient of correlation |
|------------------------|--|--|---|-------------------------------|
| JSS 001-4 (chip) | (2.5)* | $2.70_4 \pm 0.09_5$ | -0.03_2 | 0.9962 |
| JSS 003-4 (chip) | 6 | $6.20_6 \pm 0.06_7$ | -0.00_2 | 0.9996 |
| JSS 1201-1 (chip) | 5 | $5.88_9 \pm 0.20_8$ | -0.03_4 | 0.9962 |
| Leco 502-231 (chip) | <8 | $2.19_6 \pm 0.11_4$ | $+0.00_6$ | 0.9951 |
| Mairon HP (plate) | — | $2.24_2 \pm 0.06_9$ | -0.02_1 | 0.9973 |
| A-Iron (plate) | — | $1.42_2 \pm 0.08_1$ | $+0.02_3$ | 0.9888 |

$n = 10$.

*, non-certified value.

iron were determined and the relationship between the sample mass and the analytical amounts of carbon is shown in Fig. 7. The linear relationship between the analytical amount of carbon and the sample mass was obtained in the sample mass between 0.25 and 1.3 g, and the intercepts of *Y*-axis were good agreement by zero in all used samples.

Analytical results of trace amounts of carbon in high-purity iron samples are listed in Table 3. The certified values in all used JSS samples and the analytical values were good agreement, respectively. The obtained analytical amounts of carbon were very precise, and carbon blank values are zero in all used samples.

4. Conclusion

In order to develop a procedure for highly sensitive and highly precise determination of trace amounts of carbon, the authors investigated about removal method of analytical carbon blank value caused from an oxygen gas, a ceramic crucible and an accelerator. Carbon species contained in the oxygen gas were removed with purification. Carbon species contained in the ceramic crucible for combustion were removed with heating at 1623 K for more than 20 min. Moreover, carbon species contained in the accelerator was removed with heating at 1003 K for 15 min and stirring every 5 min during heating. Therefore, the carbon blank value caused from instruments could be completely removed.

Next, the authors determined trace amounts of carbon in six kinds of high-purity iron samples in changed the sample mass according to the proposed procedure, after then, the relationships between the sample mass and the analytical carbon amounts were plotted. In all employed samples, linear rela-

tionships between the sample mass and the analytical amount of carbon were respectively obtained in the sample mass between 0.25 and 1.3 g. Moreover, the intercepts of *Y*-axis were good agreement at zero. Therefore, the proposed method is useful and suitable for determination of trace amounts of carbon less than $\mu\text{g}\cdot\text{g}^{-1}$ level in high-purity iron.

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